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(54) Film for retaining freshness of vegetables and fruits.

(57) Provided is a film for retaining freshness of vegetables and fruits which comprises a synthetic resin film, a microporous resin film and a water-absorbing layer interposed between both said films, said microporous resin film having a maximum pore diameter not larger than 30 microns and a moisture permeability not lower than 100 g/m^2/24 hr.

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Exhibit 8

low, that is, its ability to absorb water and moisture and release moisture is extremely poor.

Thus, as to the film for retaining the freshness of vegetables and fruits, studies have heretofore been made about synthetic resin films which control the concentration of oxygen and that of carbon dioxide, or about packages endowed with a water absorbing function by the use of water-absorbing polymers, or about packages with water-absorbing polymers received therein. However, those are not effective to a satisfactory extent, involving problems such as leaking out of water-absorbing polymers or poor water-absorbability.

It is the object of the present invention to provide a film for retaining the freshness of vegetables and fruits which film has overcome the above-mentioned problems of the prior art.

Summary of the Invention

Having made extensive studies for achieving the above object, the present inventors accomplished the present invention.

The present invention resides in a freshness retaining film comprising a synthetic resin film, a microporous resin film and a water-absorbing layer interposed between said films, characterized in that the said microporous resin film has a maximum pore diameter not larger than 30 µm and a moisture permeability not lower than 100 g/m^2/24 hr.

In the freshness retaining film for vegetables and fruits of the present invention, the synthetic resin film controls the concentrations of oxygen and that of carbon dioxide, while the combiniation of a water-absorbing layer and a specific microporous resin film absorbs moisture evaporated from vegetables and fruits. In addition, the freshness retaining film of the present invention exhibits the following effects.

(i) There is no exudation of a water-absorbing polymer used.

(ii) Superior in heat-sealability.

(iii) Delamination does not occur even after absorption of water, preventing exudation of the water-absorbing polymer and preventing direct contact of the water-absorbing polymer with vegetables and fruits.

In case of dewing on the film surface, water is absorbed promptly, so there is attained a satisfactory water and moisture absorbing effect even under a high humidity condition.

Since water-drops are not formed on the film, the surface of the film is dry, not wetting vegetables and fruits.

When the package interior is in an excess humid condition, even if the moisture evaporated from vegetables or fruits adheres as water-drops to the film surface, the water-drops will be absorbed promptly. On the other hand, in a lower humidity condition than required, that is, in a dry condition, moisture is released promptly for immediate shift to a humidity condition necessary for retaining the freshness of vegetables and fruits, and it is possible to control the humidity so as to maintain such humidity condition.

Detailed Description of the Invention

The synthetic resin film used in the present invention is required to have a carbon dioxide concentration in a package in the range of 0.5% to 10% and an oxygen concentration in the package not higher than 18%, preferably in the range of 2% to 15%, though somewhat different depending on the kind and quantity of vegetables or fruits.

More specifically, it is desirable to use a synthetic resin film having a carbon dioxide permeability at 25°C of not lower than 5,000 ml/m^2/24 hr, preferably in the range of 5,000 to 200,000 ml/m^2/hr, more preferably 5,000 to 10,000 ml/m^2/24 hr, and an oxygen permeability at 25°C not lower than 3,000 ml/m^2/24 hr, preferably in the range of 3,000 to 500,000 ml/m^2/24 hr, more preferably 3,000 to 19,000 ml/m^2/24 hr. Examples are polyethylene, polypropylene, polystyrene and ethylene-vinyl acetate copolymer films. These synthetic resin films are preferably so-called non-porous films.

The thickness of the synthetic resin film used in the invention and exemplified above is not specially limited, but from the standpoint of carbon dioxide and oxygen permeability, strength, processability such as heat melt-bonding, and handleability, it is preferable that the thickness of the synthetic resin film be in the range of 5 to 50 µm, particularly 20 to 40 µm. A suitable synthetic resin film may be selected from those available commercially.

The water-absorbing polymer used in the present invention is water-insoluble and has a water absorbability not less than thirty times its own weight. Preferred examples are a starch-polyacrylonitrile copolymer which is disclosed in Japanese Patent Publication No. 43395/1974, a crosslinked polyalkylene oxide disclosed in Japanese Patent Publication No. 39672/1976, a saponified vinyl ester - ethylenically unsaturated carboxylic acid copolymer disclosed in Japanese Patent Publication No. 13495/1978, a self-crosslinking polyacrylate obtained by a reversed-phase suspension polymerization process disclosed in Japanese Patent Publication No. 30710/1979, the reaction product of a polyvinyl alcohol type polymer and a cyclic anhydride disclosed in Japanese Patent Laid Open No. 20093/1979, and a crosslinked polyacrylate disclosed in Japanese Patent Laid Open No. 84305/1980.

The amount of the water-absorbing polymer to be used differs depending on the kind and quantity of vegetables or fruits, packaged condition, state of preservation, etc., but usually it is in the range of 0.001% to 1%, preferably 0.005% to 0.5%,

based on the weight of vegetables or fruits. It is preferably in the range of 1 to 100 grams per square meter of the film.

Further, for the purpose of adsorbing gas such as ethylene, there may be used together with the

Further, the water-absorbing polymer or the adhesive may be used in the form of a partial pattern according to the bonding force between the synthetic resin film and the microporous resin film as well as the water and moisture absorbing ability.

In the freshness retaining film obtained in the above manner, the oxygen permeability thereof is not lower 2,000 ml/m²/24 hr/atm, preferably in the range of 2,000 to 200,000 ml/m²/24 hr/atm more preferably 2,000 to 15,000 ml/m²/24 hr/atm.

If the oxygen permeability is lower than 2,000 ml/m²/24 hr/atm, the carbon dioxide concentration in package will become higher due to breathing of the inside agricultural food, resulting in that some particular kinds of agricultural foods may cause a carbon dioxide trouble. On the other hand, if the oxygen permeability exceeds 200,000 ml/m²/24 hr/atm, it is impossible to suppress the breathing of the inside agricultural food to a satisfactory extent, that is, the freshness of the agricultural food cannot be retained over a long period.

As the bonding method for obtaining a package to keep the freshness of vegetables and fruits using the freshness retaining film of the present invention, it is desirable to use an ultrasonic sealing method, heat sealing method, or impulse sealing method.

How to use the freshness retaining film of the present invention is not specially limited. Not only in the form of a bag to seal vegetables or fruits therein but also the film may be in the form of a cloth wrapper to package and preserve vegetables or fruits like a handkerchief package, or a corrugated cardboard case may be lined with the film, or the film may be put into a corrugated cardboard case together with vegetables or fruits and used at the time of preservation or distribution. Further, the film of the present invention may be attached to a window portion of a container. It is used so that the microporous film side comes into contact with vegetables or fruits.

The present invention will be described below in detail in terms of working examples, but the invention is not limited thereto.

How to Prepare the Freshness Retaining Film of Present Invention

There were used the following (a) synthetic resin films, (b) water-absorbing layer materials and (c) micro-porous resin film.

(a) Synthetic Resin Films

There were used polyethylene films having a density of 0.927 g/cm³, an MI of 2.0 and thicknesses of 15 and 30 µm, and an ethylene-vinyl acetate (vinyl acetate 28%) copolymer film having a thickness of 10 µm which are commercially available. Their oxygen permeability (O_2P; ml/m²/24 hr/atm) and carbon dioxide permeability (CO_2P; ml/m²/24 hr/atm) at 25°C are as follows:

Polyethylene films:

Thickness	O_2P	CO_2P
15 µ	14,000	33,000
30 µ	6,000	23,000

Ethylene-vinyl acetate copolymer film:

10 µ	20,000	60,000

(b) Water-absorbing Polymer

A starch-polyacrylic acid graft copolymer (Sanwet IM-300, a product of Sanyo Chemical Industries, Ltd.). Also, as an urethanic adhesive there was used (EPS-75A), a product of Dainippon Ink & Chemicals, Inc.

(c) Microporous Resin Film

150 parts by weight of barium sulfate was added for 100 parts by weight of a linear low-density polyethylene, followed by melting and forming into film and subsequent stretching to obtain a film having a thickness of 30 µm, a moisture permeability of 1,400 g/m²/24 hr and a maximum pore diameter of 7.5 µm. Further, in order to increase the water absorbing speed, a 10 wt% solution of a phenolic surfactant (MTN-F684, a product of Marubishi Yuka K.K.) in isopropyl alcohol was applied onto the film surface by a dipping method and thus a hydrophilicizing treatment was performed.

Preparation Example - 1

100 parts by weight of the urethanic adhesive and 100 parts by weight of the water-absoring polymer (b) were mixed together at low speed in a homomixer and the resultant mixture was applied to the surface of the 15 µm thick polyethylene film (a) to result in 8 g/m² in terms of the amount of the water-absorbing polymer by means of a gravure coating roll to form a water-absorbing layer.

Thereafter, the microporous resin film (c) was laminated to the water-absorbing layer to obtain a freshness retaining film according to the present invention, which film was found to have an oxygen permeability of 13,000 ml/m²/24 hr/atm.

marked detericration of the commercial value.

Example - 5

673 g of carrots were washed with water, then water was drained off by shaking the carrots merely up and down, thereafter the carrots were sealed into a 2.5-liter package formed using the freshness retaining film obtained in Preparation Example-2, and preserved at 20°C for one month. As a result, condensate was not observed at all, nor was observed any of such abnormal conditions as change of color and drying.

Comparative Example - 4

Using the same 30 µm polyethylene film as that used in Comparative Example-2, there was conducted the same test as in Example-4. After one month of preservation, condensate was observed at many points on the inner surface of the package and something like mold was observed at the neck portions of some of the carrots; besides, there occurred a change of color partially. Thus, a marked deterioration of the commercial value was recognized.

Example - 6

A corrugated cardboard case (280 x 370 x 118.5 mm) was lined with the freshness retaining film obtained in Preparation Example-2. 6 kg of green asparagus was washed with water, then water was drained off by shaking the asparagus merely up and down and thereafter the green asparagus was packed into the corrugated cardboard case lined with the freshness retaining film, which case was transported at 20°C from Hokkaido to Tokyo. The results are as set forth in Table 2.

Comparative Example - 5

6 kg of green asparagus was washed with water, then water was drained off by shaking merely up and down and thereafter the asparagus was packed into a corrugated cardboard case (280 x 370 x 118.5 mm), which case transported at 20°C from Hokkaido to Tokyo. The results are as set forth in Table 2.

The present invention uses a freshness retaining film having the construction described above as a film for packaging vegetables and fruits, whereby the following effects are attained.

① The synthetic resin film permits controlling the concentration of carbon dioxide and that of oxygen gas to values suitable for vegetables or fruits to be preserved.

② Condensate, or dew water, formed within a package can be absorbed and removed by the water-absorbing polymer.

When the humidity in a package is high, the moisture in the package is absorbed by the combination of the water-absorbing polymer with a specific microporous resin film, while in a lower humidity condition than required, that is, in a dry condition, the water and moisture which have been absorbed are released. Thus, by repeating the absorption of water and moisture and the release thereof it is possible to keep constant the internal humidity of the package.

③ The presence of a microporous film having a maximum pore diameter not larger than 30 prevents the water-absorbing polymer from oozing out from the film surface and thus prevents the film surface from becoming wet. Moreover, because of a good heat-sealability it is possible to prevent delamination of the sealed portion and leakage of the water-absorbing polymer after the absorption of water and moisture.

Further, since water-drops are not formed on the film surface, the inside vegetables or fruits are not wet, resulting in that the freshness thereof can be retained over a long period.

In the preservation of vegetables and fruits using the freshness retaining film of the present invention exhibiting the above effects, there was recognized a very superior freshness and quality retaining effect.

The combiniation of the water-absorbing layer with a specific microporous film is advantageous in that in an excess humid condition, even if the moisture evaporated from vegetables or fruits adheres as drops to the film surface, the water-drops will be absorbed promptly, while in a dry condition, the absorbed water and moisture will be released promptly.

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EUROPEAN SEARCH REPORT

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EP 89 30 8386

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4410578 (MILLER) * column 1, lines 19 - 25 * * column 3, line 41 - column 4, line 66; figure 6 * ---	1, 3	B32B27/00 B32B5/18 B65D81/26 B65D85/34 B65D65/40
Y	US-A-4453320 (ZIMMERMANN) * claims 1, 2 * ---	1, 3	
A	GB-A-2031849 (PFIZER INC.) * page 1, lines 5 - 9 * * page 2, lines 1 - 32 * * page 2, lines 91 - 113; figure * ---	1	
A	US-A-4715918 (LANG) * column 2, line 64 - column 3, line 19 * * column 5, lines 46 - 49 * * column 6, lines 11 - 24; figure 1 * ---	1, 3, 4	
A	US-A-4662877 (WILLIAMS) * column 1, line 65 - column 2, line 3 * * column 3, lines 26 - 34; figure 3 * -----	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B32B B65D81

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 AUGUST 1990	IBARROLA TORRES O.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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